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An improved protocol for the preparation of 5,11-dialkyl-6,12-di(hetero)aryl-5,11-dihydroindolo[3,2-*b*]carbazoles and synthesis of their new 2,8-dicyano- / 2,8-bis(benzo[*d*]thiazol-2-yl)-substituted derivatives

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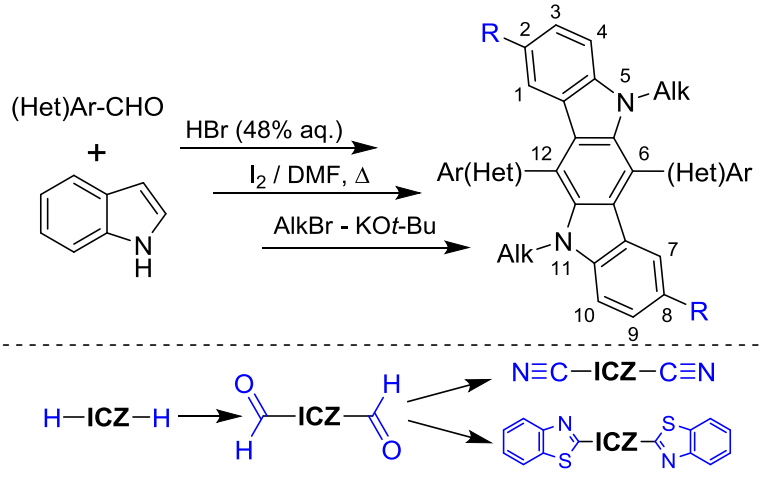
Abstract

A number of 5,11-dialkyl-6,12-di(hetero)aryl-5,11-dyhydroindolo[3,2-*b*]carbazoles has been synthesized by modified method based on HBr catalyzed condensation of (hetero)aromatic aldehydes with indole in MeCN solution affording 5,6,11,12-tetrahydroindolo[3,2-*b*]carbazoles, that have been aromatized with I_2 in DMF solution for 1 h at reflux, followed by alkylation of 5,11-dihydro compounds. New 2,8-dicyano- (10 examples) as well as 2,8-bis(benzo[*d*]thiazol-2-yl)-substituted (5 examples) derivatives of these 5,11-dyhydroindolo[3,2-*b*]carbazoles have been obtained through their initial C2,8-formylation, followed by treatment of dialdehydes with excess of hydroxylamine and dehydration of the formed aldoximes with acetic anhydride or by interaction with excess of 2-aminothiophenol in DMSO solution, respectively.



Keywords: Indolo[3,2-*b*]carbazole, indole, aldehydes, N-heteroacenes, benzo[*d*]thiazoles, nitriles

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Introduction

5,11-Dihydroindolo[3,2-*b*]carbazoles (indolo[3,2-*b*]carbazoles, ICZs) are an important class of fused nitrogen-containing heterocycles (N-heteroarenes) with ladder-type structure, whose representatives attracted a considerable attention of researchers thanks to their promising applications in biology[1-5] and material science.[6-8] In respect to latter topic, ICZ compounds have been used as photo- and electroactive components of organic electronic devices. In general, this is due to the fact that π-conjugated and rigid planar indolo[3,2-*b*]carbazole ring system has a number of useful optical and electronic properties, as well as high thermal, photo- and electrochemical stability as well as high resistance toward oxidation by air oxygen.[9-13] Thus, a number of ICZ derivatives, bearing (hetero)aromatic substituents at main scaffold, have been applied as electroluminescent and charge-transport materials for organic light-emitting diodes (OLEDs)[14-18] and organic field-effect transistors (OFETs),[19-22] as well as light-harvesting dyes for organic photovoltaics (OPVs).[23-26] In particular, some structures of such materials are presented in Figure 1.

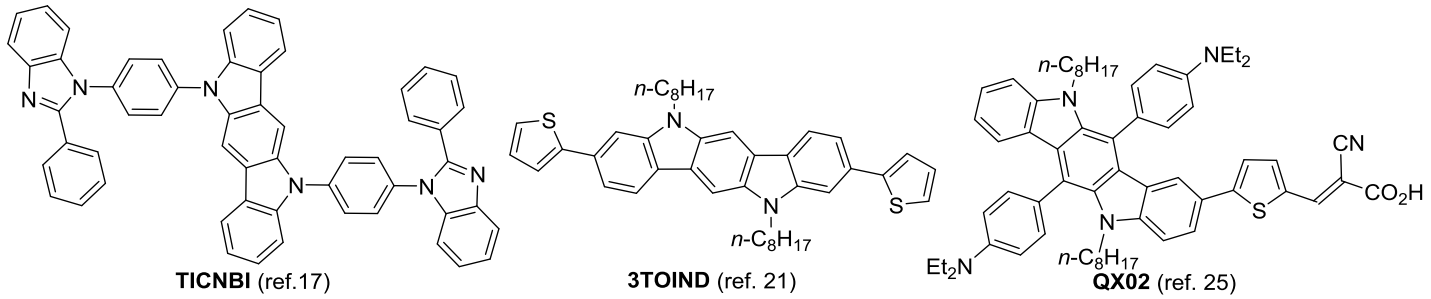


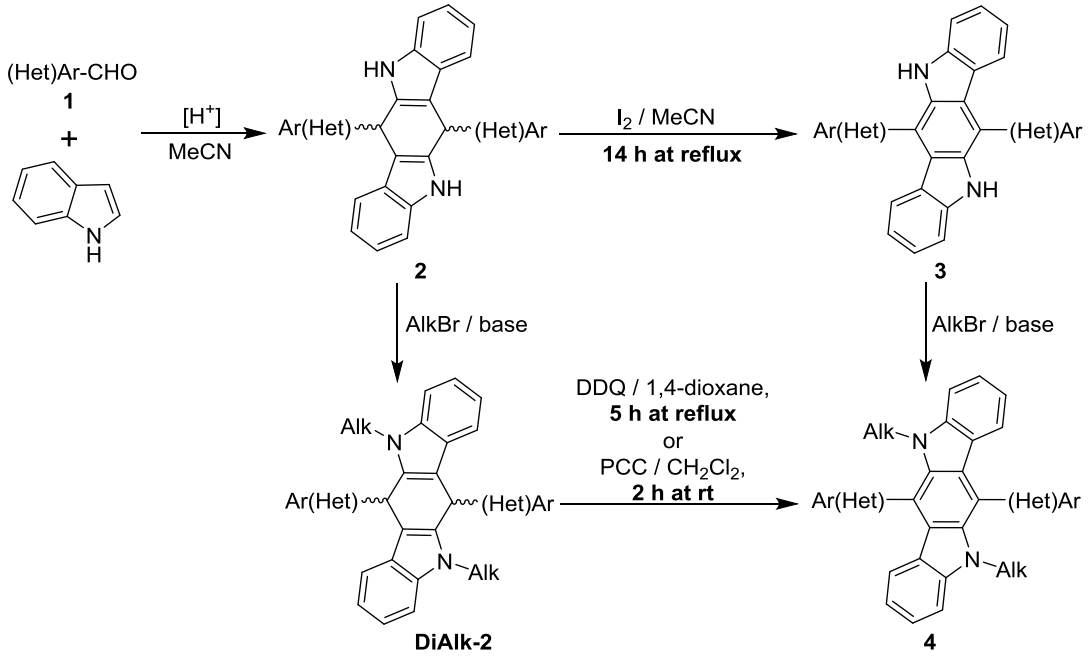
Figure 1. Structures of indolo[3,2-*b*]carbazole-based semiconductors.

In this relation, 6,12-di(hetero)aryl-substituted indolo[3,2-*b*]carbazoles are of particular interest as chemical substrates with high synthetic potential since there are wide opportunities for regioselective modification of their structure.[8] Furthermore, these ICZs are conveniently available, because they can be easily obtained by reaction of (hetero)aromatic aldehydes with indoles in acidic conditions, followed by oxidation of intermediate 5,6,11,12-tetrahydroICZs. Thus, we have recently described a number of convenient synthetic procedures for regioselective formylation, acylation, aroylation and nitration of 5,11-dialkyl-6,12-di(hetero)aryl-substituted indolo[3,2-*b*]carbazoles at C-2 and C-8 positions, and demonstrated usefulness of the obtained functional ICZ derivatives as building blocks for construction of more complex π-conjugated and fused molecules.[27-31]

Result and Discussion

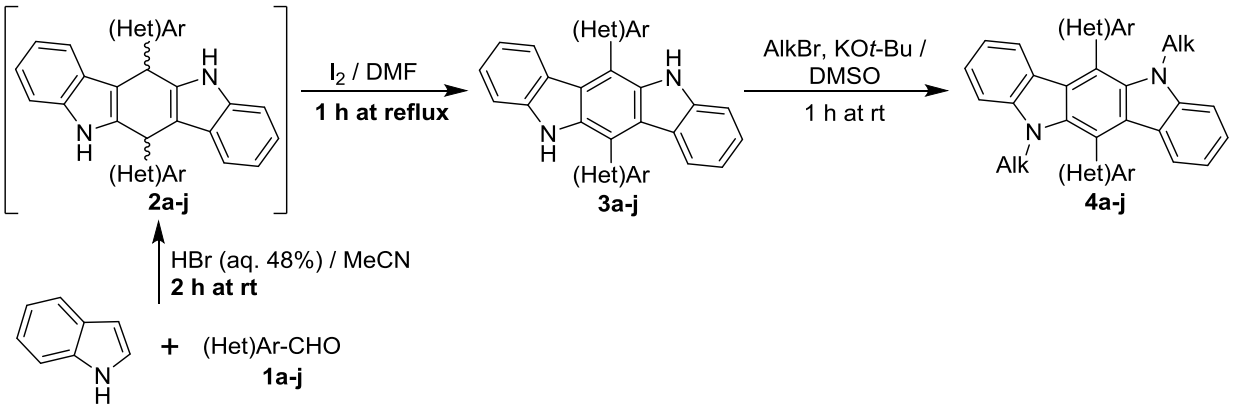
In this paper, we wish to report practically improved method for preparation of 5,11-dialkyl-6,12-di(hetero)aryl-substituted indolo[3,2-*b*]carbazoles, modified procedure for their formylation as well as some new synthetic applications of the obtained 2,8-diformyl derivatives. Thus, indolo[3,2-*b*]carbazoles **4** can be readily prepared in three steps through two synthetic routes (Scheme 1), which have been previously described in the literature. In particular, 5,6,11,12-tetrahydroICZs **2** have been initially formed by condensation of aldehydes **1** with indole in the presence of mineral acid (e.g. 57% aq. HI) on the first step. Next, *N*-alkylation of compounds **2** has afforded intermediates **DiAlk-2**, which have further been aromatized by treatment with DDQ in 1,4-dioxane at reflux for 5 h or with pyridinium chlorochromate (PCC) in CH_2Cl_2 at

ambient temperature for 2 h, to give desired products **4**.[27] Thus, current way to ICZs **4** has included aromatization step with DDQ or PCC, which are moderately toxic and not eco-friendly oxidative reagents, *e.g.* PCC produced Cr-containing slugs as by-products. Compared to DDQ and PCC, the use of I_2 as reagent for aromatization of 5,6,11,12-tetrahydroICZs **2** in the alternative synthetic way to ICZs **4** is more attractive option.[32,33] However, this process requires prolonged refluxing of reaction mixture for 14 h, since compounds **2** and **3** have very poor solubility in acetonitrile (Scheme 1). Moreover, purification, including column chromatography, of intermediates **DiAlk-2** and **3** is required in both synthetic routes to ICZs **4**.



Scheme 1. Synthesis of 5,11-dialkyl-6,12-di(hetero)aryl-substituted ICZs.

During our studies of 5,11-dihydroindolo[3,2-*b*]carbazoles, a number of valuable improvements in preparation method of ICZs **4** have been made, since these compounds have generally been used by us as starting ICZ substrates in our researches. Firstly, it has been found, that not only 57% aq. HI[32] or equimolar mixture of 48% aq. HBF_4 and *n*-Bu_4NI,[27] but also 48% aq. HBr can catalyze condensation of indole with aldehydes **1** to form 5,6,11,12-tetrahydroICZs **2** (Scheme 2). Moreover, current process proceeds fairly quickly,



Scheme 2. Modification in synthesis of ICZs **3** and their 5,11-dialkyl derivatives **4**.

because the main amounts of intermediates **2a-j** precipitated during 2 h since the beginning of reaction, and the further increase of the reaction time does not substantially increase yields of compounds **2**. Secondly, we have found that *N,N*-dimethylformamide (DMF) can be successfully used as solvent for aromatization of intermediates **2** with I_2, since these compounds have very good solubility in DMF at high temperature.

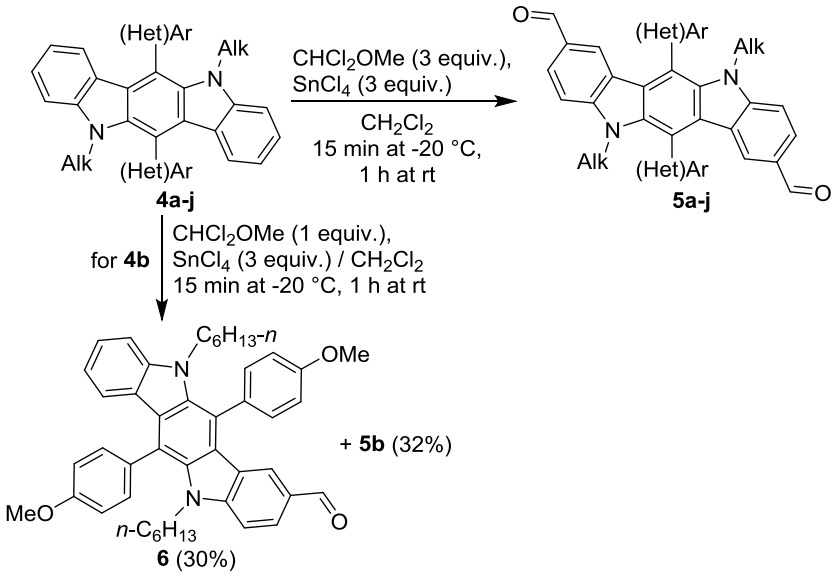
Table 1. Scope and yields of ICZs **3** and **4**

Entry	ICZs **3** or **4**	(Het)Ar	Alk	Yield (%) [a]
1	**3a**	phenyl	-	36
2	**3b**	4-methoxyphenyl	-	72
3	**3c**	3,4,5-trimethoxyphenyl	-	60
4	**3d**	4-chlorophenyl	-	54
5	**3e**	thiophen-2-yl		48
6	**3f**	benzo[*b*]thiophen-2-yl	-	68
7	**3g**	4-hexyloxyphenyl	-	55
8	**3h**	4-octylphenyl	-	23
9	**3i**	4-fluorophenyl	-	43
10	**3j**	4-isopropylphenyl	-	42
11	**4a**	phenyl	*n*-C_6H_{13}	84
12	**4b**	4-methoxyphenyl	*n*-C_6H_{13}	76
13	**4c**	3,4,5-trimethoxyphenyl	*n*-C_6H_{13}	79
14	**4d**	4-chlorophenyl	*n*-C_6H_{13}	57
15	**4e**	thiophen-2-yl	*n*-C_6H_{13}	71
16	**4f**	phenyl	*n*-$C_{12}H_{25}$	87
17	**4g**	4-methoxyphenyl	*n*-$C_{12}H_{25}$	67
18	**4h**	3,4,5-trimethoxyphenyl	*n*-$C_{12}H_{25}$	66
19	**4i**	4-chlorophenyl	*n*-$C_{12}H_{25}$	50
20	**4j**	thiophen-2-yl	*n*-$C_{12}H_{25}$	82

[a] Yields of ICZs **3a-j** based on starting aldehydes **1a-j** and indole.

Thus, a series of ICZs **3** has been obtained starting from 5,6,11,12-tetrahydro derivatives **2**, without purification in the previous step, by heating their DMF solutions with I_2 (1 equiv.) for 1 h at reflux (Scheme 2, Table 1) instead of 14 h according to the known procedure with acetonitrile. Pure products **3** have been obtained by simple filtration of cooled reaction mixtures and one more crystallization of crude samples from DMF. It should be noted, that current procedure for preparation of ICZs **3** is fully applicable for their multigram scale syntheses. Further alkylation of ICZ compounds **3** proceeded smoothly at their treatment with long-chain alkyl bromides, namely 1-bromohexane and 1-bromododecane, in the presence of potassium *tert*-butoxide in dry DMSO solution for 1 h, affording derivatives **4** (Table 1, entries 11-20). The latter ICZ compounds have been used for preparation of their 2,8-diformyl-substituted derivatives by the Rieche formylation. In particular, the treatment of ICZs **4** with commercial dichloromethyl methyl ether (3 equiv.) in the presence of $SnCl_4$ in dry CH_2Cl_2 at -20 °C for 15 min and then 1 h at room temperature was found to give dialdehydes **5** in good yields (Scheme 3, Table 2). The current yields of dialdehydes **5b** and **5e** are fully comparable with the yields obtained by our previous procedure for formylation of ICZs **4** with dichloromethyl *n*-pentyl ether,[27] that needed to be prepare from *n*-pentyl fromiate. In its turn, dialdehyde **5a** has previously been obtained only via

the double Br/Li exchange on corresponding 2,8-dibromoICZ with *n*-BuLi, followed by treatment of the formed organodilithium compound with excess of dry DMF.[33] In addition, monoaldehyde **6** has been synthesized by treatment of compound **4b** with stoichiometric amounts of dichloromethyl methyl ether (1 equiv.) in the same manner. However, further formylation of **6**, as unwanted reaction, has been also observed under these conditions forming dialdehyde **5b**, thereby not full conversion of starting substrate **4b** has been observed. Thus, target monoaldehyde **6** has been separated from side product **5b** and starting material **4b** only using column chromatography.



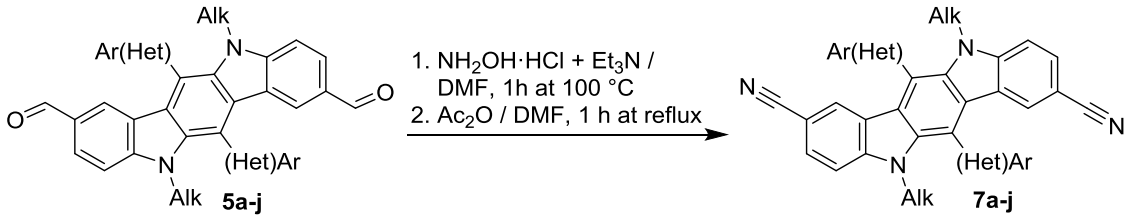
Scheme 3. C2- and C2,8-formylation of ICZs **4**

Table 2. Scope and yields of 2,8-diformyl-substituted ICZs **5**

Entry	Dialdehydes **5**	(Het)Ar	Alk	Yield of **5** (%)
1	**5a**	phenyl	*n*-C_6H_{13}	91
2	**5b**	4-methoxyphenyl	*n*-C_6H_{13}	92
3	**5c**	3,4,5-trimethoxyphenyl	*n*-C_6H_{13}	55
4	**5d**	4-chlorophenyl	*n*-C_6H_{13}	89
5	**5e**	thiophen-2-yl	*n*-C_6H_{13}	76
6	**5f**	phenyl	*n*-$C_{12}H_{25}$	84
7	**5g**	4-methoxyphenyl	*n*-$C_{12}H_{25}$	72
8	**5h**	3,4,5-trimethoxyphenyl	*n*-$C_{12}H_{25}$	51
9	**5i**	4-chlorophenyl	*n*-$C_{12}H_{25}$	81
10	**5j**	thiophen-2-yl	*n*-$C_{12}H_{25}$	88

Taking into consideration the fact that the obtained dialdehydes **5** are of utmost interest as functional building blocks for further construction of target structures, two novel applications of these substrates for synthesis of ICZ-based molecules have been elaborated during this study. Thus, a series of new 2,8-dicyano-substituted ICZs **7a-j** has been obtained by treatment of dialdehydes **5a-j** with excess of hydroxylamine hydrochloride and triethylamine in DMF solution for 1 h at 100 °C, that has caused smooth formation of corresponding aldoximes, followed by addition of acetic anhydride and heating of reaction mixture at reflux

for 1 h, to perform dehydration of the formed aldoximes (Scheme 4, Table 3). On the one hand, introduction of cyano-groups into structure of poly(hetero)aromatics can be useful for tuning their optical and electrical characteristics. For instance, some cyano-substituted carbazoles have recently been regarded as effective host materials for blue phosphorescent OLEDs (PhOLEDs)[34,35] or electroluminescent materials for OLEDs.[36] On the other hand, cyano-containing compounds can be interesting as chemicals for synthesis, since CN-groups are readily able to undergo further transformations. It should be also noted, that dinitriles **7** are the first representatives of the CN-equipped ICZ scaffold, since there are no reports in the literature on synthesis of any such matters to the best of our knowledge.

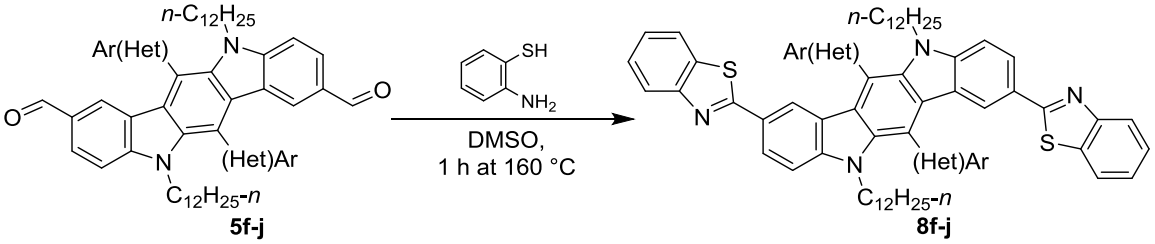


Scheme 4. Synthesis of 2,8-dicyano-substituted ICZ derivatives **7**.

Table 3. Scope and yields of 2,8-dicyano-substituted ICZs **7**

Entry	Dinitriles **7**	(Het)Ar	Alk	Yield of **7** (%)
1	**7a**	phenyl	*n*-C_6H_{13}	71
2	**7b**	4-methoxyphenyl	*n*-C_6H_{13}	73
3	**7c**	3,4,5-trimethoxyphenyl	*n*-C_6H_{13}	60
4	**7d**	4-chlorophenyl	*n*-C_6H_{13}	83
5	**7e**	thiophen-2-yl	*n*-C_6H_{13}	70
6	**7f**	phenyl	*n*-$C_{12}H_{25}$	80
7	**7g**	4-methoxyphenyl	*n*-$C_{12}H_{25}$	80
8	**7h**	3,4,5-trimethoxyphenyl	*n*-$C_{12}H_{25}$	83
9	**7i**	4-chlorophenyl	*n*-$C_{12}H_{25}$	86
10	**7j**	thiophen-2-yl	*n*-$C_{12}H_{25}$	70

It is well known that benzo[*d*]thiazole is often used as a mild π-acceptor part for design of various photo- and electroactive compounds. In particular, several examples of effective luminescent and electroluminescent materials based on benzo[*d*]thiazole-indolo[3,2-*b*]carbazole[37-39] and benzo[*d*]thiazole-carbazole[40-42] dyads have been recently described in the literature. In this context, dialdehydes **5** have been also used for preparation of new symmetric 2,6,8,12-tetra(hetero)aryl-substituted ICZs, bearing benzo[*d*]thiazol-2-yl moiety at C-2 and C-8 (BTICZs). Thus, substrates **5f-j** have smoothly reacted with 2-aminothiophenol in DMSO solution at 160 °C for 1 h affording compounds **8f-j** (Scheme 5, Table 4). Dialdehydes **5a-e**, bearing *n*-hexyl groups at both nitrogen atoms of their ICZ core, have also been tested in this reaction and corresponding derivatives **8** have been formed. However, all attempts at purification and characterization of the latter species have been fruitless, since these matters have very poor solubility in most commonly used organic solvents. Compared to this, compounds **8f-j**, supported with long *n*-dodecyl chains, have been easily purified by crystallization from DMF.



Scheme 5. Synthesis of 2,8-bis(benzo[*d*]thiazol-2-yl)-substituted ICZ derivatives **8**.

Table 4. Scope and yields of BTICZs **8**

Entry	BTICZs **8**	(Het)Ar	Yield of **8** (%)
1	**8f**	phenyl	83
2	**8g**	4-methoxyphenyl	84
3	**8h**	3,4,5-trimethoxyphenyl	80
4	**8i**	4-chlorophenyl	93
5	**8j**	thiophen-2-yl	91

Conclusions

We have made some practical improvements for the preparation of indolo[3,2-*b*]carbazoles, bearing (hetero)aromatic fragments at C-6 and C-12 and long aliphatic chains at N-5 and N-11, as well as synthesized their new 2,8-dicyano- and 2,8-bis(benzo[*d*]thiazol-2-yl)-substituted derivatives through primary C2,8-formylation of these ICZ substrates and following transformations of the obtained dialdehydes. First of all, ICZ compounds, namely 2,8-unsubstituted, 2,8-diformyl and 2,8-dycyano derivatives, reported herein are of interest as intermediates for further chemical developments, including design of new semiconducting materials based on them. At the same time, firstly obtained 2,8-bis(benzo[*d*]thiazol-2-yl) or 2,8-dicyano ICZs can be independently considered as potential candidates for optoelectronic applications.

Experimental Section

General. Analytical studies were carried out using equipment of the Center for Joint Use "Spectroscopy and Analysis of Organic Compounds" at the Postovsky Institute of Organic Synthesis of the Russian Academy of Sciences (Ural Division). ^{1}H and ^{13}C NMR spectra were obtained on a Bruker DRX-400 and AVANCE-500 spectrometers at ambient temperature with TMS as the internal standard. Elemental analysis was carried on a Eurovector EA 3000 automated analyzer. Mass spectrometry was performed using a Bruker maXis Impact HD spectrometer. Melting points were determined on Boetius combined heating stages and were not corrected. All solvents used were dried and distilled per standard procedures. The ^{13}C NMR spectra of indolo[3,2-*b*]carbazoles **3** could not be determined due to a poor solubility of these compounds in a majority of deuterated solvents.

General procedure for preparation of 6,12-di(hetero)aryl-5,11-dihydroindolo[3,2-*b*]carbazoles (3a-j). An appropriate (het)aromatic aldehyde **1** (0.1 mol) and indole (11.7 g, 0.1 mol) were dissolved in MeCN (150 mL) and 48% aq. HBr (1.15 mL, 10 mmol) was added in one portion to this solution at the intense stirring, herewith an immediate staining of the solution to deep red was observed, and precipitation of intermediate **2** was started approximately after 15 min. The resulting mixture was stirred at room temperature for 2 h and precipitate of **2** was filtered, washed with MeCN (4×20 mL) and dried. Crude compound **2** was dissolved in DMF (150 mL) at 150 °C and I_2 (25.4 g, 0.1 mol) was added to this solution in four portions. Then, the reaction mixture was stirred and heated at reflux for 1h, after that it was cooled to room temperature. The obtained precipitate was filtered and dried. Crude substance was crystallized from DMF (60-80 mL) to afford analytically pure product **3**, that was filtered, washed with warm EtOH (2×20 mL) and finally dried at 120 °C.

Benzo[*b*]thiophen-2-carbaldehyde **1f**, 4-hexyloxybenzaldehyde **1g** and 4-octylbenzaldehyde **1h** and were taken in amounts of 5 mmol for preparation of corresponding products **3f**-**3h**. Thus, indole (590 mg, 5 mmol), 48% aq. HBr (0.06 mL, 0.5 mmol), I_2 (1.27 g, 5 mmol) and proportionally decreased volumes of solvents were used in these experiments.

6,12-Diphenyl-5,11-dihydroindolo[3,2-*b*]carbazole (3a). Light-yellow powder, yield 7.42 g (36%), mp > 360 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.53 (s, 2H), 7.77 – 7.61 (m, 10H), 7.44 (d, *J* 8.1 Hz, 2H), 7.28 – 7.20 (m, 2H), 7.05 (d, *J* 7.9 Hz, 2H), 6.85 – 6.77 (m, 2H). ICZ **3a** was previously described in the literature and its analytical data are identical to the reported data.[32]

6,12-Bis(4-methoxyphenyl)-5,11-dihydroindolo[3,2-*b*]carbazole (3b). Light-yellow powder, yield 16.93 g (72%), mp > 360 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.46 (s, 2H), 7.60 (d, *J* 7.7 Hz, 4H), 7.43 (d, *J* 7.9 Hz, 2H), 7.30 – 7.21 (m, 6H), 7.15 (d, *J* 8.2 Hz, 2H), 6.83 (t, *J* 7.6 Hz, 2H), 3.94 (s, 6H). ICZ **3b** was previously described in the literature and its analytical data are identical to the reported data.[32]

6,12-Bis(3,4,5-trimethoxyphenyl)-5,11-dihydroindolo[3,2-*b*]carbazole (3c). Yellow microcrystals, yield 17.75 g (60%), mp > 360 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.60 (s, 2H), 7.47 (d, *J* 7.9 Hz, 2H), 7.32 – 7.24 (m, 4H), 6.94 (s, 4H), 6.90 (t, *J* 7.4 Hz, 2H), 3.88 (s, 6H), 3.82 (s, 12H). Anal. Calcd for $C_{36}H_{32}N_2O_6$: C, 73.45; H, 5.48; N, 4.76. Found: C, 73.35; H, 5.53; N, 5.01.

6,12-Bis(4-chlorophenyl)-5,11-dihydroindolo[3,2-*b*]carbazole (3d). Light-yellow microcrystals, yield 12.94 g (54%), mp > 360 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.63 (s, 2H), 7.78 (d, *J* 8.4 Hz, 4H), 7.71 (d, *J* 8.4 Hz, 4H), 7.43 (d, *J* 8.0 Hz, 2H), 7.31 – 7.24 (m, 2H), 7.12 (d, *J* 7.7 Hz, 2H), 6.91 – 6.84 (m, 2H). Anal. Calcd for $C_{30}H_{18}Cl_2N_2$: C, 75.48; H, 3.80; N, 5.87; Found: C, 75.45; H, 3.87; N, 6.03.

6,12-Di(thiophen-2-yl)-5,11-dihydroindolo[3,2-*b*]carbazole (3e). White powder, yield 10.1 g (48%), mp > 360 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.77 (s, 1H), 7.96 (dd, *J* 5.1, 1.1 Hz, 2H), 7.52 – 7.45 (m, 4H), 7.42 (dd, *J* 3.4, 1.1 Hz, 2H), 7.30 (dd, *J* 11.1, 4.1 Hz, 2H), 7.15 (d, *J* 7.9 Hz, 2H), 6.95 – 6.87 (m, 2H). ICZ **3e** was previously described in the literature and its analytical data are identical to the reported data.[32]

6,12-Bis(benzo[*b*]thiophen-2-yl)-5,11-dihydroindolo[3,2-*b*]carbazole (3f). Light-yellow powder, yield 890 mg (68%) starting from aldehyde **1f** (810 mg, 5 mmol), mp > 360 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.00 (s, 2H), 8.19 (d, *J* 7.1 Hz, 2H), 8.09 (d, *J* 7.2 Hz, 2H), 7.81 (s, 2H), 7.58 – 7.50 (m, 4H), 7.46 (d, *J* 8.0 Hz, 2H), 7.34 – 7.27 (m, 4H), 6.93 – 6.86 (m, 2H). Anal. Calcd for $C_{34}H_{20}N_2S_2$: C, 78.43; H, 3.87; N, 5.38; S, 12.31; Found: C, 78.44; H, 3.97; N, 5.54; S, 12.45.

6,12-Bis(4-hexyloxyphenyl)-5,11-dihydroindolo[3,2-*b*]carbazole (3g). Light-yellow powder, yield 840 mg (55%) starting from aldehyde **1g** (1.03 g, 5 mmol), mp 239-240 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.33 (s, 2H), 7.58 (d, *J* 8.5 Hz, 4H), 7.45 (d, *J* 8.0 Hz, 2H), 7.30 – 7.22 (m, 6H), 7.18 (d, *J* 7.9 Hz, 2H), 6.87 – 6.80 (m, 2H), 4.17 (t, *J* 6.5 Hz, 4H), 1.90 – 1.81 (m, 4H), 1.59 – 1.50 (m, 4H), 1.46 – 1.36 (m, 8H), 0.95 (t, *J* 7.0 Hz, 6H). Anal. Calcd for $C_{42}H_{40}N_2O_4$: C, 82.86; H, 7.28; N, 4.60; Found: C, 82.95; H, 7.30; N, 4.53.

6,12-Bis(4-octylphenyl)-5,11-dihydroindolo[3,2-*b*]carbazole (3h). Light-yellow powder, yield 364 mg (23%) starting from aldehyde **1h** (1.09 g, 5 mmol), mp 196-197 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.35 (s, 2H), 7.60 (d, *J* 7.9 Hz, 4H), 7.53 (d, *J* 8.0 Hz, 4H), 7.46 (d, *J* 8.0 Hz, 2H), 7.24 (t, *J* 7.6 Hz, 2H), 7.09 (d, *J* 7.9 Hz, 2H), 6.79 (t, *J* 7.5 Hz, 2H), 2.83 (t, *J* 7.5 Hz, 4H), 1.86 – 1.74 (m, 4H), 1.54 – 1.25 (m, 20H), 1.00 – 0.80 (m, 6H). Anal. Calcd for $C_{46}H_{52}N_2$: C, 87.29; H, 8.28; N, 4.43; Found: C, 87.47; H, 8.45; N, 4.43.

6,12-Bis(4-fluorophenyl)-5,11-dihydroindolo[3,2-*b*]carbazole (3i). Light-yellow powder, yield 9.56 g (43%), mp > 360 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.58 (s, 2H), 7.75 – 7.68 (m, 4H), 7.59 – 7.51 (m, 4H), 7.43 (d, *J* 8.1 Hz, 2H), 7.29 – 7.23 (m, 2H), 7.07 (d, *J* 7.9 Hz, 2H), 6.89 – 6.82 (m, 2H). Anal. Calcd for $C_{30}H_{18}F_2N_2$: C, 81.07; H, 4.08; N, 6.30; Found: C, 81.28; H, 4.20; N, 6.35.

6,12-Bis(4-isopropylphenyl)-5,11-dihydroindolo[3,2-*b*]carbazole (3j). Light-yellow powder, yield 10.35 g (42%), mp > 360 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.47 (s, 2H), 7.64 – 7.56 (m, 8H), 7.45 (d, *J* 8.0 Hz, 2H), 7.26 – 7.20 (m, 2H), 7.08 (d, *J* 8.0 Hz, 2H), 6.83 – 6.77 (m, 2H), 3.13 (hept, *J* 6.9 Hz, 2H), 1.41 (d, *J* 6.9 Hz, 12H). Anal. Calcd for $C_{36}H_{32}N_2$: C, 87.77; H, 6.55; N, 5.69; Found: C, 87.76; H, 6.60; N, 5.75.

General procedure for alkylation of ICZ derivatives 3a-e. An appropriate ICZ **3** (25 mmol) was dissolved in dry DMSO (100 mL) at heating, and then the solution was cooled to room temperature at the continuous stirring under an argon atmosphere, to form a fine suspension of ICZ substrate. Potassium *tert*-butoxide (8,4 g, 75 mmol) was added to this suspension in one portion, obtaining muddy green colored solution. This solution was dropwise treated with 1-bromohexane (10.5 mL, 75 mmol) or 1-bromododecane (18 mL, 75 mmol) and the resulting mixture was stirred at room temperature for 1 h. After that, warm water (50 mL) was added to the mixture and the precipitate was filtered and washed wish *i*-PrOH or *n*-BuOH (2×20 mL) to remove aliphatic impurities. Crude material was crystallized from DMF (50-60 mL) to give analytically pure product **4**, that was filtered, washed with EtOH (2×20 mL) and then dried at 120 °C.

5,11-Dihexyl-6,12-diphenyl-5,11-dihydroindolo[3,2-*b*]carbazole (4a). Light-yellow crystals, yield 12.11 g (84%), mp 203-204 °C. ^{1}H NMR (400 MHz, C_6D_6) δ 7.65 – 7.57 (m, 4H), 7.36 – 7.29 (m, 8H), 7.19 (d, *J* 8.2 Hz, 2H), 7.02 – 6.95 (m, 4H), 3.75 – 3.69 (m, 4H), 1.49 – 1.36 (m, 4H), 1.18 – 1.07 (m, 4H), 1.03 – 0.92 (m, 4H), 0.85 – 0.73 (m, 10H). ICZ **4a** was previously described in the literature and its analytical data are identical to the reported data.[33]

5,11-Dihexyl-6,12-bis(4-methoxyphenyl)-5,11-dihydroindolo[3,2-*b*]carbazole (4b). Light-yellow crystals, yield 12.14 g (76%), mp 199-200 °C. ^{1}H NMR (500 MHz, C_6D_6) δ 7.57 – 7.50 (m, 4H), 7.39 – 7.33 (m, 2H), 7.23 (d, *J* 8.1 Hz, 2H), 7.19 (d, *J* 7.8 Hz, 2H), 7.04 – 7.00 (m, 2H), 6.99 – 6.94 (m, 4H), 3.88 – 3.77 (m, 4H), 3.42 (s, 6H), 1.53 – 1.41 (m, 4H), 1.18 – 1.09 (m, 4H), 1.04 – 0.95 (m, 2H), 0.92 – 0.77 (m, 5H). ICZ **4b** was previously described in the literature and its analytical data are identical to the reported data.[27]

5,11-Dihexyl-6,12-bis(3,4,5-trimethoxyphenyl)-5,11-dihydroindolo[3,2-*b*]carbazole (4c). Light-yellow crystals, yield 14.95 g (79%), mp 192-193 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.37 (m, 2H), 7.33 (d, *J* 8.1 Hz, 2H), 6.96 – 6.89 (m, 6H), 6.81 (d, *J* 8.0 Hz, 2H), 4.08 (s, 6H), 3.92 – 3.84 (m, 16H), 1.69 – 1.60 (m, 4H), 1.32 – 1.24 (m, 4H), 1.24 – 1.17 (m, 4H), 1.10 – 1.02 (m, 4H), 0.89 (t, *J* 7.2 Hz, 6H). ICZ **4c** was previously described in the literature and its analytical data are identical to the reported data.[28]

6,12-Bis(4-chlorophenyl)-5,11-dihexyl-5,11-dihydroindolo[3,2-*b*]carbazole (4d). Light-yellow crystals, yield 9.2 g (57%), mp 225-226 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.57 (m, 8H), 7.39 – 7.31 (m, 2H), 7.30 – 7.26 (m, 2H), 6.92 – 6.83 (m, 2H), 6.59 (d, *J* 7.9 Hz, 2H), 3.85 – 3.72 (m, 4H), 1.54 – 1.44 (m, 4H), 1.29 – 1.20 (m, 4H), 1.16 – 1.08 (m, 4H), 1.00 – 0.91 (m, 4H), 0.88 (t, *J* 7.2 Hz, 6H). ^{13}C NMR (101 MHz, C_6D_6) δ 143.2, 137.9, 134.5, 133.0, 132.5, 129.4, 126.1, 123.6, 123.2, 122.8, 118.9, 117.4, 108.9, 44.7, 31.7, 28.9, 26.7, 22.9, 14.2. Anal. Calcd for $C_{42}H_{42}Cl_2N_2$: C, 78.12; H, 6.56; N, 4.34; Found: C, 77.83; H, 6.73; N, 4.33.

5,11-Dihexyl-6,12-di(thiophen-2-yl)-5,11-dihydroindolo[3,2-*b*]carbazole (4e). Light-yellow crystals, yield 10.45 g (71%), mp 216-217 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (dd, *J* 5.2, 1.1 Hz, 2H), 7.40 – 7.29 (m, 8H), 6.96 – 6.89 (m, 2H), 6.65 (d, *J* 7.9 Hz, 2H), 1.70 – 1.59 (m, 4H), 1.31 – 1.16 (m, 8H), 1.13 – 1.03 (m, 4H), 0.87 (t, *J* 7.2 Hz, 6H). ICZ **4c** was previously described in the literature and its analytical data are identical to the reported data.[27]

5,11-Didodecyl-6,12-diphenyl-5,11-dihydroindolo[3,2-*b*]carbazole (4f). Light-yellow crystals, yield 16.21 g (87%), mp 121-122 °C. ^{1}H NMR (500 MHz, C_6D_6) δ 7.66 – 7.61 (m, 4H), 7.37 – 7.31 (m, 8H), 7.22 (d, *J* 8.2 Hz, 2H), 7.04 – 6.96 (m, 4H), 3.79 – 3.70 (m, 4H), 1.53 – 1.44 (m, 4H), 1.35 – 1.20 (m, 24H), 1.20 – 1.13 (m, 4H), 1.09 – 1.01 (m, 4H), 0.92 (t, *J* 6.9 Hz, 6H), 0.88 – 0.80 (m, 4H). ICZ **4f** was previously described in the literature and its analytical data are identical to the reported data.[31]

5,11-Didodecyl-6,12-bis(4-methoxyphenyl)-5,11-dihydroindolo[3,2-*b*]carbazole (4g). Light-yellow crystals, yield 13.49 g (67%), mp 136-137 °C. ^{1}H NMR (500 MHz, C_6D_6) δ 7.60 – 7.53 (m, 4H), 7.38 – 7.34 (m, 2H), 7.25 (d, *J* 8.0 Hz, 2H), 7.21 (d, *J* 8.0 Hz, 2H), 7.05 – 7.01 (m, 2H), 7.01 – 6.96 (m, 4H), 3.92 – 3.80 (m, 4H), 3.44 (s, 6H), 1.58 – 1.47 (m, 4H), 1.36 – 1.22 (m, 24H), 1.17 (dt, *J* 13.3, 6.5 Hz, 4H), 1.11 – 1.03 (m, 4H), 0.96 – 0.86 (m, 10H). ICZ **4g** was previously described in the literature and its analytical data are identical to the reported data.[31]

5,11-Didodecyl-6,12-bis(3,4,5-trimethoxyphenyl)-5,11-dihydroindolo[3,2-*b*]carbazole (4h). Light-yellow crystals, yield 15.27 g (66%), mp 126-127 °C. ^{1}H NMR (500 MHz, C_6D_6) δ 7.42 – 7.36 (m, 4H), 7.29 (d, *J* 8.1 Hz, 2H), 7.04 (t, *J* 7.6 Hz, 2H), 6.96 (s, 4H), 4.08 (s, 6H), 3.97 – 3.89 (m, 4H), 3.39 (s, 12H), 1.66 – 1.56 (m, 4H), 1.37 – 1.17 (m, 28H), 1.16 – 1.08 (m, 4H), 1.03 – 0.95 (m, 4H), 0.95 – 0.89 (m, 6H). ^{13}C NMR (126 MHz, C_6D_6) δ 154.8, 143.3, 139.3, 134.5, 133.2, 126.0, 123.9, 123.4, 123.2, 119.0, 118.8, 108.9, 107.9, 61.0, 55.8, 44.8, 32.3, 30.1, 30.1, 30.0, 29.9, 29.83, 29.76, 29.7, 27.4, 23.1, 14.3. Anal. Calcd for $C_{60}H_{80}N_2O_6$: C, 77.88; H, 8.71; N, 3.03; Found: C, 77.53; H, 8.78; N, 3.07.

6,12-Bis(4-chlorophenyl)-5,11-didodecyl-5,11-dihydroindolo[3,2-*b*]carbazole (4i). Light-yellow crystals, yield 10.18 g (50%), mp 148-149 °C. ^{1}H NMR (500 MHz, C_6D_6) δ 7.39 – 7.27 (m, 10H), 7.19 (d, *J* 8.2 Hz, 2H), 7.02 – 6.94 (m, 4H), 3.72 – 3.59 (m, 4H), 1.44 – 1.26 (m, 28H), 1.22 – 1.13 (m, 4H), 1.07 – 0.99 (m, 4H), 0.93 (t, *J* 6.8 Hz, 6H), 0.87 – 0.78 (m, 4H). ^{13}C NMR (126 MHz, C_6D_6) δ 143.2, 137.9, 134.5, 133.0, 132.4, 129.4, 126.1, 123.5, 123.2, 122.8, 118.9, 117.3, 108.9, 44.7, 32.3, 30.13, 30.11, 30.03, 30.0, 29.8, 29.6, 29.0, 27.1, 23.1, 14.4. Anal. Calcd for $C_{54}H_{66}Cl_2N_2$: C, 79.68; H, 8.17; N, 3.44 Found: C, 79.69; H, 8.24; N, 3.47.

5,11-Didodecyl-6,12-di(thiophen-2-yl)-5,11-dihydroindolo[3,2-*b*]carbazole (4j). Light-yellow crystals, yield 15.52 g (82%), mp 120-121 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* 4.9 Hz, 2H), 7.41 – 7.27 (m, 8H), 7.00 – 6.88 (m, 2H), 6.65 (d, *J* 8.0 Hz, 2H), 4.10 – 3.73 (m, 4H), 1.70 – 1.58 (m, 4H), 1.36 – 1.17 (m, 32H), 1.14 – 1.01 (m, 4H), 0.88 (t, *J* 6.7 Hz, 6H). ICZ **4j** was previously described in the literature and its analytical data are identical to the reported data.[31]

General procedure for C2,8-formylation of ICZ derivatives 4a-j. Dichloromethyl methyl ether (4.1 mL, 45 mmol) was added dropwise to a stirred solution of appropriate ICZ compound **4** (15 mmol) and $SnCl_4$ (5.3 mL, 45 mmol) in dry CH_2Cl_2 (100 mL) at -20 °C during 15 min. After that, the resulting dark colored solution was stirred at room temperature for 1 h, and then poured into ice-cold water (200 mL) with conc. HCl (5 mL). The obtained biphasic mixture was intensively stirred for 30 min and the CH_2Cl_2 layer was separated, washed with water (50 mL), 5% KOH aqueous solution (2×25 mL) and dried with anhydrous $CaCl_2$. The solvent was removed under reduced pressure and the residue was crystallized from DMF (50 mL). The analytically pure product **5** was filtered, washed with EtOH (3×15 mL) and then dried at 120 °C.

5,11-Dihexyl-6,12-diphenyl-5,11-dihydroindolo[3,2-*b*]carbazole-2,8-dicarbaldehyde (5a). Yellow crystals, yield 8.64 g (91%), mp 280-281 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.59 (s, 2H), 7.93 (dd, *J* 8.6, 1.4 Hz, 2H), 7.76 –

7.66 (m, 10H), 7.35 (d, *J* 8.6 Hz, 2H), 6.86 (d, *J* 1.4 Hz, 2H), 3.94 – 3.86 (m, 4H), 1.60 – 1.52 (m, 4H), 1.28 – 1.19 (m, 4H), 1.12 (dt, *J* 9.2, 7.1 Hz, 4H), 0.96 – 0.88 (m, 4H), 0.86 (t, *J* 7.3 Hz, 6H). Dialdehyde **5a** was previously described in the literature and its analytical data are identical to the reported data.[33]

5,11-Dihexyl-6,12-bis(4-methoxyphenyl)-5,11-dihydroindolo[3,2-*b*]carbazole-2,8-dicarbaldehyde (5b). Yellow crystals, yield 9.56 g (92%), mp 257-258 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.64 (s, 2H), 7.95 (dd, *J* 8.6, 1.3 Hz, 2H), 7.57 (d, *J* 8.6 Hz, 4H), 7.35 (d, *J* 8.6 Hz, 2H), 7.24 (d, *J* 8.6 Hz, 4H), 6.98 (d, *J* 1.3 Hz, 2H), 4.02 (s, 6H), 3.98 – 3.90 (m, 4H), 1.62 – 1.52 (m, 4H), 1.28 – 1.19 (m, 4H), 1.18 – 1.08 (m, 4H), 1.03 – 0.92 (m, 4H), 0.87 (t, *J* 7.2 Hz, 6H). Dialdehyde **5a** was previously described in the literature and its analytical data are identical to the reported data.[27]

5,11-Dihexyl-6,12-bis(3,4,5-trimethoxyphenyl)-5,11-dihydroindolo[3,2-*b*]carbazole-2,8-dicarbaldehyde (5c). Yellow crystals, yield 6.71 g (55%), mp 266-267 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.71 (s, 2H), 7.99 (dd, *J* 8.6, 1.2 Hz, 2H), 7.41 (d, *J* 8.6 Hz, 2H), 7.10 (s, 2H), 6.90 (s, 4H), 4.10 (s, 6H), 4.05 – 3.98 (m, 4H), 3.87 (s, 12H), 1.71 – 1.62 (m, 4H), 1.29 – 1.22 (m, 4H), 1.21 – 1.14 (m, 4H), 1.11 – 1.02 (m, 4H), 0.86 (t, *J* 7.2 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.2, 154.2, 145.8, 138.8, 132.9, 132.6, 128.1, 127.7, 126.0, 123.1, 122.5, 118.9, 109.0, 107.0, 61.5, 56.3, 44.8, 31.5, 29.5, 26.5, 22.5, 13.9. HRMS (+ESI): Calcd. for $C_{50}H_{57}N_2O_8$ m/z 813.4109 $[M+H]^+$, found m/z 813.4107 $[M+H]^+$.

6,12-Bis(4-chlorophenyl)-5,11-dihexyl-5,11-dihydroindolo[3,2-*b*]carbazole-2,8-dicarbaldehyde (5d). Yellow crystals, yield 9.37 g (89%), mp 300-301 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.66 (s, 2H), 7.97 (d, *J* 8.6 Hz, 2H), 7.72 (d, *J* 8.2 Hz, 4H), 7.63 (d, *J* 8.4 Hz, 4H), 7.37 (d, *J* 8.4 Hz, 2H), 6.95 (s, 2H), 3.99 – 3.77 (m, 4H), 1.59 – 1.50 (m, 4H), 1.29 – 1.21 (m, 4H), 1.18 – 1.10 (m, 4H), 1.03 – 0.94 (m, 4H), 0.89 (t, *J* 7.2 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.4, 146, 135.9, 135.2, 133.2, 131.6, 129.7, 128.1, 127.6, 126.0, 123.1, 122.4, 117.9, 109.1, 44.9, 31.4, 28.9, 26.4, 22.5, 14.0. Anal. Calcd for $C_{44}H_{42}Cl_2N_2O_2$: C, 75.31; H, 6.03; N, 3.99; Found: C,75.14; H,5.98; N,4.16.

5,11-Dihexyl-6,12-di(thiophen-2-yl)-5,11-dihydroindolo[3,2-*b*]carbazole-2,8-dicarbaldehyde (5e). Yellow crystals, yield 7.35 g (76%), mp 242-243 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.74 (s, 2H), 7.99 (dd, *J* 8.6, 1.4 Hz, 2H), 7.79 (dd, *J* 5.2, 0.9 Hz, 2H), 7.45 (dd, *J* 5.2, 3.5 Hz, 2H), 7.41 (d, *J* 8.6 Hz, 2H), 7.38 (d, *J* 2.7 Hz, 2H), 7.03 – 6.97 (m, 2H), 4.30 – 3.86 (m, 4H), 1.75 – 1.63 (m, 4H), 1.33 – 1.17 (m, 8H), 1.15 – 1.05 (m, 4H), 0.89 (t, *J* 7.0 Hz, 6H). Dialdehyde **5e** was previously described in the literature and its analytical data are identical to the reported data.[27]

5,11-Didodecyl-6,12-diphenyl-5,11-dihydroindolo[3,2-*b*]carbazole-2,8-dicarbaldehyde (5f). Yellow crystals, yield 10.11 g (84%), mp 176-177 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.59 (s, 2H), 7.93 (dd, *J* 8.6, 1.5 Hz, 2H), 7.77 – 7.65 (m, 10H), 7.35 (d, *J* 8.6 Hz, 2H), 6.85 (d, *J* 1.5 Hz, 2H), 3.99 – 3.83 (m, 4H), 1.63 – 1.51 (m, 4H), 1.36 – 1.07 (m, 32H), 0.96 – 0.85 (m, 10H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.5, 145.9, 137.6, 133.1, 130.1, 129.4, 128.8, 128.6, 127.9, 125.7, 123.2, 122.7, 119.0, 108.8, 44.8, 31.9, 29.6, 29.59, 29.48, 29.46, 29.3, 29.1, 28.9, 26.6, 22.7, 14.1. Anal. Calcd for $C_{56}H_{68}N_2O_2$: C, 83.95; H, 8.56; N, 3.50; Found: C, 83.93; H, 8.75; N, 3.47.

5,11-Didodecyl-6,12-bis(4-methoxyphenyl)-5,11-dihydroindolo[3,2-*b*]carbazole-2,8-dicarbaldehyde (5g). Yellow crystals, yield 9.31 g (72%), mp 180-181 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.64 (s, 2H), 7.94 (dd, *J* 8.6, 1.5 Hz, 2H), 7.57 (d, *J* 8.6 Hz, 4H), 7.35 (d, *J* 8.6 Hz, 2H), 7.23 (d, *J* 8.6 Hz, 4H), 6.98 (d, *J* 1.5 Hz, 2H), 4.02 (s, 6H), 3.98 – 3.89 (m, 4H), 1.60 – 1.51 (m, 4H), 1.33 – 1.10 (m, 32H), 1.01 – 0.92 (m, 4H), 0.88 (t, *J* 6.8 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.5, 160.2, 145.9, 133.5, 131.2, 129.4, 128.1, 127.8, 125.5, 123.6, 122.8, 118.7, 114.8, 108.8, 55.6, 44.7, 31.9, 29.62, 29.59, 29.54, 29.51, 29.3, 29.2, 29.0, 26.7, 22.7, 14.1. Anal. Calcd for $C_{58}H_{72}N_2O_4$: C, 80.89; H, 8.43; N, 3.25; Found: C, 80.96; H, 8.43; N, 2.96.

5,11-Didodecyl-6,12-bis(3,4,5-trimethoxyphenyl)-5,11-dihydroindolo[3,2-*b*]carbazole-2,8-dicarbaldehyde (5h). Yellow crystals, yield 7.51 g (51%), mp 182-183 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.71 (s, 2H), 7.99 (dd, *J*

8.6, 1.4 Hz, 2H), 7.41 (d, *J* 8.6 Hz, 2H), 7.10 (d, *J* 1.4 Hz, 2H), 6.90 (s, 4H), 4.10 (s, 6H), 4.04 – 3.97 (m, 4H), 3.87 (s, 12H), 1.71 – 1.61 (m, 4H), 1.32 – 1.16 (m, 32H), 1.10 – 1.00 (m, 4H), 0.88 (t, *J* 6.8 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.3, 154.3, 145.9, 138.9, 133.0, 132.6, 128.1, 127.8, 126, 123.1, 122.5, 119.0, 109.0, 107.0, 61.5, 56.4, 44.8, 31.9, 29.7, 29.6, 29.53, 29.45, 29.34, 29.27, 26.9, 22.6, 14.1 (1 signal ($2C_{Alkyl}$) was not found due to overlapping peaks). Anal. Calcd for $C_{62}H_{80}N_2O_8$: C, 75.89; H, 8.22; N, 2.85; Found: C, 76.00; H, 8.24; N, 3.08.

6,12-Bis(4-chlorophenyl)-5,11-didodecyl-5,11-dihydroindolo[3,2-*b*]carbazole-2,8-dicarbaldehyde (5i). Yellow crystals, yield 10.57 g (81%), mp 237-238 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.66 (s, 2H), 7.97 (dd, *J* 8.6, 1.4 Hz, 2H), 7.72 (d, *J* 8.3 Hz, 4H), 7.63 (d, *J* 8.3 Hz, 4H), 7.37 (d, *J* 8.6 Hz, 2H), 6.95 (d, *J* 1.3 Hz, 2H), 3.96 – 3.80 (m, 4H), 1.63 – 1.48 (m, 4H), 1.31 – 1.12 (m, 32H), 1.02 – 0.92 (m, 4H), 0.88 (t, *J* 6.8 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.3, 145.9, 135.9, 135.2, 133.1, 131.6, 129.7, 128.1, 127.5, 126.0, 123.1, 122.4, 117. 9, 109.1, 44.9, 31.9, 29.6, 29.6, 29.51, 29.49, 29.3, 29.2, 29.0, 26.7, 22.7, 14.1. Anal. Calcd for $C_{56}H_{66}Cl_2N_2O_2$: C, 77.31; H, 7.65; N, 3.22; Found: C, 77.39; H, 7.52; N, 3.48.

5,11-Didodecyl-6,12-di(thiophen-2-yl)-5,11-dihydroindolo[3,2-*b*]carbazole-2,8-dicarbaldehyde (5j). Yellow crystals, yield 10.73 g (88%), mp 160-161 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.76 (s, 2H), 8.01 (dd, *J* 8.6, 1.5 Hz, 2H), 7.81 (dd, *J* 5.2, 1.0 Hz, 2H), 7.47 (dd, *J* 5.2, 3.4 Hz, 2H), 7.43 (d, *J* 8.6 Hz, 2H), 7.41 – 7.38 (m, 2H), 7.03 (s, 2H), 4.22 – 3.94 (m, 4H), 1.76 – 1.66 (m, 4H), 1.35 – 1.23 (m, 32H), 1.18 – 1.06 (m, 4H), 0.90 (t, *J* 6.8 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.5, 145.9, 137.4, 134.4, 128.5, 128.3, 128.1, 127.9, 127.7, 126.3, 124.7, 122.2, 111.8, 109.1, 44.8, 31.9, 29.6, 29.50, 29.48, 29.4, 29.3, 29.3, 29.2, 26.8, 22.7, 14.1. Anal. Calcd for $C_{52}H_{64}N_2O_2S_2$: C, 76.80; H, 7.93; N, 3.44; Found: C, 76.75; H, 7.78; N, 3.48.

Procedure for C2-formylation of ICZ 4b. Derivative **4b** (1 g, 1.57 mmol) and $SnCl_4$ (0.55 mL, 4.7 mmol) were dissolved and stirred in dry CH_2Cl_2 (50 mL). Dichloromethyl methyl ether (180 mg, 1.57 mmol) in dry CH_2Cl_2 (20 mL) was dropped to the reaction mixture at -20 °C during 15 min and the resulting solution was stirred at room temperature for 1 h. The reaction mixture was treated with water (40 mL) and conc. HCl (1 mL), organic layer was separated, washed with water (20 mL), 5% KOH aqueous solution (15 mL) and dried with anhydrous $CaCl_2$. The CH_2Cl_2 extract was evaporated under reduced pressure to give desired product **6** in the mixture with unreacted compound **4b** and dialdehyde **5b**. This mixture was separated using column chromatography on silica by eluting with benzene to isolate starting material **4b** and next with CH_2Cl_2 for separation of monoaldehyde **6** and dialdehyde **5b**. It has been obtained ICZ **4b** (345 mg, 0.54 mmol), monoaldehyde **6** (205 mg, 0.31 mmol, yield 30% based on the reacted **4b**) and dialdehyde **5b** (226 mg, 0.33 mmol, yield 32% based on the reacted **4b**).

5,11-Dihexyl-6,12-bis(4-methoxyphenyl)-5,11-dihydroindolo[3,2-*b*]carbazole-2-carbaldehyde (6). Yellow crystals, yield 205 mg (30%), mp 158-159 °C. ^{1}H NMR (500 MHz, C_6D_6) δ 9.94 (s, 1H), 8.08 (dd, *J* 8.5, 1.2 Hz, 1H), 7.51 – 7.47 (m, 5H), 7.38 – 7.34 (m, 1H), 7.22 (d, *J* 8.2 Hz, 1H), 7.05 (d, *J* 8.5 Hz, 1H), 7.04 – 6.94 (m, 6H), 3.89 – 3.82 (m, 2H), 3.74 – 3.68 (m, 2H), 3.47 (s, 3H), 3.41 (s, 3H), 1.51 – 1.44 (m, 2H), 1.43 – 1.35 (m, 2H), 1.18 – 1.08 (m, 4H), 1.01 – 0.95 (m, 4H), 0.89 – 0.78 (m, 10H). ^{13}C NMR (126 MHz, C_6D_6) δ 190.4, 160.5, 160.2, 146.3, 143.3, 134,0, 133.6, 131.9, 131.7, 130.8, 130.7, 128.9, 127.5, 126.22, 126.16, 124.6, 123.91, 123.88, 123.7, 123.2, 119.0, 118.9, 118.8, 115.1, 114.7, 109.04, 108.96, 55.2, 54.9, 44.9, 44.7, 31.71, 31.69, 29.1, 29.0, 26.8, 26.7, 22.9, 14.2 (2 signal ($4C_{Alkyl}$) were not found due to overlapping peaks). Anal. Calcd for $C_{45}H_{48}N_2O_3$: C, 81.29; H, 7.28; N, 4.21; Found: C, 81.34; H, 7.38; N, 4.01.

General procedure for synthesis of 2,8-dicyano-substituted ICZ derivatives (7a-j). An appropriate dialdehyde **5** (1 mmol) was added to a solution of hydroxylamine hydrochloride (280 mg, 4 mmol) and Et_3N (0.7 mL, 5

mmol) in dry DMF (15 mL) and the obtained mixture was stirred and heated at 100 °C for 1 h. After that time, acetic anhydride (0.95 mL, 10 mmol) was added to this solution and the reaction mixture was stirred and heated to reflux for another 1 h. The resulting solution was cooled and diluted with EtOH (15 mL) and the formed precipitate was collected by filtration. Crude material was crystallized from DMF (5 mL) to give analytically pure product **7**, that was filtered, washed with EtOH (2×5 mL) and dried at 120 °C.

5,11-Dihexyl-6,12-diphenyl-5,11-dihydroindolo[3,2-*b*]carbazole-2,8-dicarbonitrile (7a). Bright-yellow crystals, yield 445 mg (71%), mp 324-325 °C. ^{1}H NMR (500 MHz, C_6D_6) δ 7.39 – 7.35 (m, 4H), 7.32 (dd, *J* 8.5, 1.5 Hz, 2H), 7.25 – 7.20 (m, 6H), 6.98 (d, *J* 1.5 Hz, 2H), 6.75 (d, *J* 8.5 Hz, 2H), 3.59 – 3.47 (m, 4H), 1.30 – 1.21 (m, 4H), 1.15 – 1.07 (m, 4H), 0.97 – 0.88 (m, 4H), 0.82 (t, *J* 7.3 Hz, 6H), 0.71 – 0.63 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.1, 137.1, 133.0, 129.9, 129.6, 129.2, 129.0, 127.4, 122.8, 122.6, 120.7, 119.0, 109.0, 100.7, 44.7, 31.3, 28.8, 26.2, 22.5, 13.9. Anal. Calcd for $C_{44}H_{42}N_4$: C, 84.31; H, 6.75; N, 8.94; Found: C, 84.31; H, 6.98; N, 9.05.

5,11-Dihexyl-6,12-bis(4-methoxyphenyl)-5,11-dihydroindolo[3,2-*b*]carbazole-2,8-dicarbonitrile (7b). Bright-yellow crystals, yield 500 mg (73%), mp 293-294 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* 8.5, 1.3 Hz, 1H), 7.53 (d, *J* 8.6 Hz, 4H), 7.33 (d, *J* 8.6 Hz, 2H), 7.23 (d, *J* 8.6 Hz, 4H), 6.93 (d, *J* 1.3 Hz, 2H), 4.03 (s, 6H), 3.94 – 3.82 (m, 4H), 1.59 – 1.47 (m, 4H), 1.32 – 1.21 (m, 4H), 1.20 – 1.11 (m, 4H), 1.05 – 0.93 (m, 4H), 0.89 (t, *J* 7.2 Hz, 6H). ^{1}H NMR (400 MHz, C_6D_6) δ 7.37 – 7.34 (m, 2H), 7.32 (d, *J* 8.5 Hz, 4H), 7.10 (s, 2H), 6.90 (d, *J* 8.5 Hz, 4H), 6.79 (d, *J* 8.6 Hz, 2H), 3.68 – 3.57 (m, 4H), 3.39 (s, 6H), 1.36 – 1.25 (m, 4H), 1.16 – 1.07 (m, 4H), 0.98 – 0.89 (m, 4H), 0.83 (t, *J* 7.3 Hz, 6H), 0.79 – 0.69 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.2, 144.1, 133.4, 130.9, 128.9, 128.84, 128.77, 127.3, 122.9, 120.8, 118.7, 114.9, 108.9, 100.6, 55.5, 44.6, 31.3, 28.8, 26.3, 22.5, 13.9. Anal. Calcd for $C_{45}H_{48}N_2O_3$: C, 81.29; H, 7.28; N, 4.21; Found: C, 81.34; H, 7.38; N, 4.01.

5,11-Dihexyl-6,12-bis(3,4,5-trimethoxyphenyl)-5,11-dihydroindolo[3,2-*b*]carbazole-2,8-dicarbonitrile (7c). Bright-yellow crystals, yield 484 mg (60%), mp 276-277 °C. ^{1}H NMR (400 MHz, C_6D_6) δ 7.38 – 7.33 (m, 4H), 6.85 (d, *J* 9.0 Hz, 2H), 6.79 (s, 4H), 4.15 (s, 6H), 3.84 – 3.73 (m, 4H), 3.35 (s, 12H), 1.45 – 1.34 (m, 4H), 1.18 – 1.08 (m, 4H), 1.02 – 0.93 (m, 4H), 0.89 – 0.77 (m, 10H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.3, 144.0, 139.0, 132.9, 132.1, 129.1, 127.4, 122.6, 122.5, 120.5, 118.9, 109.2, 106.7, 101.1, 61.6, 56.3, 44.7, 31.5, 29.4, 26.5, 22.5, 13.9. Anal. Calcd for $C_{50}H_{54}N_4O_6$: C, 74.42; H, 6.74; N, 6.94; Found: C, 74.19; H, 6.69; N, 6.98.

6,12-Bis(4-chlorophenyl)-5,11-dihexyl-5,11-dihydroindolo[3,2-*b*]carbazole-2,8-dicarbonitrile (7d). Bright-yellow crystals, yield 577 mg (83%), mp > 360 °C. ^{1}H NMR (400 MHz, C_6D_6) δ 7.34 (dd, *J* 8.7, 1.1 Hz, 2H), 7.23 – 7.18 (m, 4H), 7.12 – 7.06 (m, 6H), 6.74 (d, *J* 8.7 Hz, 2H), 3.48 – 3.37 (m, 4H), 1.23 – 1.07 (m, 8H), 0.95 – 0.82 (m, 10H), 0.72 – 0.62 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.18, 135.46, 135.33, 133.14, 131.30, 129.84, 129.30, 127.05, 122.49, 122.39, 120.50, 117.89, 109.24, 101.09, 44.78, 31.33, 28.78, 26.32, 22.50, 13.93. ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.1, 136.9, 134.3, 129.3, 128.5, 128.3, 128.2, 127.5, 124.1, 122.3, 120.7, 111.8, 109.3, 101.4, 44.7, 31.3, 29.2, 26.4, 22.5, 13.9. Anal. Calcd for $C_{44}H_{40}Cl_2N_4$: C, 75.96; H, 5.80; N, 8.05; Found: C, 75.69; H, 5.60; N, 8.02.

5,11-Dihexyl-6,12-di(thiophen-2-yl)-5,11-dihydroindolo[3,2-*b*]carbazole-2,8-dicarbonitrile (7e). Bright-yellow crystals, yield 447 mg (70%), mp 281-282 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, *J* 5.2, 1.1 Hz, 2H), 7.64 (dd, *J* 8.6, 1.3 Hz, 2H), 7.42 (dd, *J* 5.2, 3.4 Hz, 2H), 7.36 (d, *J* 8.6 Hz, 2H), 7.34 – 7.30 (m, 2H), 6.84 (d, *J* 1.3 Hz, 2H), 4.10 – 3.84 (m, 4H), 1.72 – 1.57 (m, 4H), 1.33 – 1.15 (m, 8H), 1.13 – 1.01 (m, 4H), 0.88 (t, *J* 7.1 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.1, 136.9, 134.3, 129.3, 128.5, 128.3, 128.2, 127.5, 124.1, 122.3, 120.7, 111.8, 109.3, 101.4, 44.7, 31.3, 29.2, 26.4, 22.5, 13.9. HRMS (+ESI): Calcd. for $C_{40}H_{39}N_4S_2$ m/z 639.2611 $[M+H]^+$, found m/z 639.2606 $[M+H]^+$.

5,11-Didodecyl-6,12-diphenyl-5,11-dihydroindolo[3,2-*b*]carbazole-2,8-dicarbonitrile (7f). Bright-yellow crystals, yield 636 mg (80%), mp 271-272 °C. ^{1}H NMR (400 MHz, C_6D_6) δ 7.43 – 7.36 (m, 4H), 7.33 (dd, *J* 8.6, 1.3 Hz, 2H), 7.28 – 7.20 (m, 6H), 6.99 (d, *J* 1.3 Hz, 2H), 6.78 (d, *J* 8.6 Hz, 2H), 3.63 – 3.46 (m, 4H), 1.37 – 1.21 (m,

28H), 1.20 – 1.11 (m, 4H), 1.05 – 0.96 (m, 4H), 0.93 (t, *J* 6.7 Hz, 6H), 0.78 – 0.68 (m, 4H). ^{13}C NMR (126 MHz, C_6D_6) δ 144.4, 137.6, 133.3, 130.1, 129.7, 129.2, 129.1, 123.4, 123.3, 120.5, 119.6, 109.4, 102.2, 44.7, 32.3, 30.07, 30.05, 29.94, 29.88, 29.8, 29.5, 29.0, 26.8, 23.1, 14.3 (1 signal ($2C_{Aryl}$) was not found due to overlapping peaks). Anal. Calcd for $C_{56}H_{66}N_4$: C, 84.59; H, 8.37; N, 7.05 Found: C, 84.53; H, 8.38; N, 7.10.

5,11-Didodecyl-6,12-bis(4-methoxyphenyl)-5,11-dihydroindolo[3,2-*b*]carbazole-2,8-dicarbonitrile (7g). Bright-yellow crystals, yield 684 mg (80%), mp 218-219 °C. ^{1}H NMR (400 MHz, C_6D_6) δ 7.37 – 7.31 (m, 6H), 7.22 (d, *J* 1.3 Hz, 2H), 6.93 (d, *J* 8.5 Hz, 4H), 6.82 (d, *J* 8.6 Hz, 2H), 3.72 – 3.62 (m, 4H), 3.42 (s, 6H), 1.40 – 1.22 (m, 28H), 1.20 – 1.12 (m, 4H), 1.07 – 0.97 (m, 4H), 0.93 (t, *J* 6.7 Hz, 6H), 0.85 – 0.76 (m, 4H). ^{13}C NMR (126 MHz, C_6D_6) δ 160.8, 144.4, 133.9, 131.3, 129.3, 129.1, 123.8, 123.6, 120.6, 119.4, 115.3, 109.4, 102.1, 55.3, 44.8, 32.3, 30.11, 30.09, 30.01, 29.97, 29.8, 29.6, 29.1, 27.0, 23.1, 14.4 (1 signal ($2C_{Aryl}$) was not found due to overlapping peaks). Anal. Calcd for $C_{58}H_{70}N_4O_2$: C, 81.46; H, 8.25; N, 6.55; Found: C, 81.20; H, 8.36; N, 6.39.

5,11-Didodecyl-6,12-bis(3,4,5-trimethoxyphenyl)-5,11-dihydroindolo[3,2-*b*]carbazole-2,8-dicarbonitrile (7h). Bright-yellow crystals, yield 810 mg (83%), mp 191-192 °C. ^{1}H NMR (500 MHz, C_6D_6) δ 7.40 – 7.33 (m, 2H), 6.86 (d, *J* 8.9 Hz, 2H), 6.81 (s, 4H), 4.16 (s, 6H), 3.86 – 3.77 (m, 4H), 3.37 (s, 12H), 1.49 – 1.41 (m, 4H), 1.37 – 1.23 (m, 24H), 1.21 – 1.13 (m, 4H), 1.10 – 1.00 (m, 4H), 0.95 – 0.84 (m, 10H). ^{13}C NMR (126 MHz, C_6D_6) δ 155.4, 144.4, 140.7, 133.5, 132.4, 129.2, 123.5, 123.3, 120.4, 119.8, 109.7, 107.7, 102.5, 61.5, 56.2, 44.9, 32.3, 30.2, 30.04, 29.98, 29.92, 29.88, 29.8, 29.7, 27.1, 23.1, 14.3 (1 signal ($2C_{Aryl}$) was not found due to overlapping peaks). HRMS (+ESI): Calcd. for $C_{62}H_{82}N_5O_6$ m/z 992.6260 $[M+NH_4]^+$, found m/z 992.6255 $[M+NH_4]^+$.

6,12-Bis(4-chlorophenyl)-5,11-didodecyl-5,11-dihydroindolo[3,2-*b*]carbazole-2,8-dicarbonitrile (7i). Bright-yellow crystals, yield 743 mg (86%), mp 310-311 °C. ^{1}H NMR (500 MHz, C_6D_6) δ 7.34 (dd, *J* 8.5, 1.0 Hz, 2H), 7.20 (d, *J* 8.2 Hz, 4H), 7.12 (d, *J* 8.2 Hz, 4H), 7.08 (s, 2H), 6.77 (d, *J* 8.5 Hz, 2H), 3.56 – 3.36 (m, 4H), 1.39 – 1.14 (m, 32H), 1.03 – 0.96 (m, 4H), 0.94 (t, *J* 6.8 Hz, 6H), 0.77 – 0.69 (m, 4H). ^{13}C NMR (126 MHz, C_6D_6) δ 144.3, 135.6, 133.4, 131.6, 130.0, 129.4, 127.5, 127.4, 123.0, 120.2, 118.4, 109.6, 102.6, 44.7, 32.3, 30.09, 30.08, 29.9, 29.8, 29.5, 29.0, 26.9, 23.1, 14.3 (2 signal ($2C_{Aryl}$ and $2C_{Alkyl}$) were not found due to overlapping peaks). Anal. Calcd for $C_{56}H_{64}Cl_2N_4$: C, 77.84; H, 7.47; N, 6.48; Found: C, 77.95; H, 7.34; N, 6.43.

5,11-Didodecyl-6,12-di(thiophen-2-yl)-5,11-dihydroindolo[3,2-*b*]carbazole-2,8-dicarbonitrile (7j). Bright-yellow crystals, yield 565 mg (70%), mp 192-193 °C. ^{1}H NMR (500 MHz, C_6D_6) δ 7.35 (dd, *J* 8.5, 1.5 Hz, 2H), 7.11 – 7.04 (m, 4H), 6.99 – 6.94 (m, 2H), 6.91 – 6.86 (m, 2H), 6.77 (d, *J* 8.5 Hz, 2H), 3.68 (t, *J* 8.3 Hz, 4H), 1.47 – 1.24 (m, 28H), 1.24 – 1.16 (m, 4H), 1.14 – 1.05 (m, 4H), 0.97 – 0.84 (m, 10H). ^{13}C NMR (126 MHz, C_6D_6) δ 144.2, 137.4, 134.5, 129.4, 128.7, 128.3, 127.7, 124.8, 122.8, 120.5, 112.2, 109.7, 102.7, 44.7, 32.3, 30.1, 30.0, 29.9, 29.8, 29.6, 29.5, 29.4, 27.0, 23.1, 14.3 (1 signal ($2C_{Aryl}$) was not found due to overlapping peaks). HRMS (+ESI): Calcd. for $C_{52}H_{63}N_4S_2$ m/z 807.4489 $[M+H]^+$, found m/z 807.4498 $[M+H]^+$.

General procedure for synthesis of 2,8-bis(benzo[*d*]thiazol-2-yl)-substituted ICZ derivatives (8f-j). 2-Aminothiophenol (0.32 mL, 3 mmol) was added to a suspension of dialdehyde **5** (1 mmol) in DMSO (15 mL) and the resulting mixture was stirred and heated at 160 °C for 1 h. After that time, it cooled to room temperature and the formed precipitate was filtered and washed with EtOH (10 mL). Crude matter was purified by crystallization form DMF (15 mL), filtered, washed with EtOH (10 mL) and dried at 120 °C to give analytically pure form of product **8**.

2,2'-(5,11-Didodecyl-6,12-diphenyl-5,11-dihydroindolo[3,2-*b*]carbazole-2,8-diyl)bis(benzo[*d*]thiazole) (8f). Orange crystals, yield 840 mg (83%), mp 196-197 °C. ^{1}H NMR (400 MHz, C_6D_6) δ 8.76 (dd, *J* 8.6, 1.5 Hz, 2H), 8.16 (d, *J* 8.0 Hz, 2H), 7.67 – 7.59 (m, 6H), 7.58 – 7.48 (m, 8H), 7.24 – 7.17 (m, 4H), 7.01 (t, *J* 7.5 Hz, 2H), 3.81 – 3.67 (m, 4H), 1.53 – 1.41 (m, 4H), 1.37 – 1.16 (m, 28H), 1.12 – 1.02 (m, 4H), 0.92 (t, *J* 6.7 Hz, 6H), 0.88 – 0.79 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.6, 154.1, 144.1, 138.0, 134.8, 132.8, 130.2, 129.4, 128.9, 125.9,

124.7, 124.3, 123.8, 123.2, 123.0, 122.96, 122.4, 121.3, 118.7, 108.7, 44.6, 31.9, 29.6, 29.58, 29.54, 29.52, 29.4, 29.2, 28.9, 26.6, 22.7, 14.1. Anal. Calcd for $C_{68}H_{74}N_4S_2$: C, 80.75; H, 7.37; N, 5.54; Found: C, 80.85; H, 7.51; N, 5.72.

2,2'-(5,11-Didodecyl-6,12-bis(4-methoxyphenyl)-5,11-dihydroindolo[3,2-*b*]carbazole-2,8-diyl)bis(benzo[*d*]-thiazole) (8g). Orange crystals, yield 900 mg (84%), mp 228-229 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* 8.2 Hz, 2H), 8.03 (d, *J* 8.2 Hz, 2H), 7.85 (d, *J* 7.7 Hz, 2H), 7.62 (d, *J* 8.6 Hz, 4H), 7.50 – 7.42 (m, 2H), 7.41 – 7.32 (m, 4H), 7.29 (d, *J* 8.6 Hz, 4H), 7.00 (d, *J* 1.5 Hz, 2H), 4.09 (s, 6H), 4.07 – 3.93 (m, 4H), 1.66 – 1.55 (m, 4H), 1.35 – 1.09 (m, 32H), 1.06 – 0.95 (m, 4H), 0.88 (t, *J* 6.8 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.8, 160.0, 154.1, 144.0, 134.7, 133.1, 131.3, 129.9, 126.0, 124.5, 124.3, 123.6, 123.3, 123.2, 123.1, 122.4, 121.2, 118.3, 114.9, 108.6, 55.5, 44.6, 31.9, 29.7, 29.64, 29.61, 29.58, 29.4, 29.2, 29.0, 26.8, 22.7, 14.1. Anal. Calcd for $C_{70}H_{78}N_4O_2S_2$: C, 78.46; H, 7.34; N, 5.23; Found: C, 78.59; H, 7.28; N, 5.54.

2,2'-(5,11-Didodecyl-6,12-bis(3,4,5-trimethoxyphenyl)-5,11-dihydroindolo[3,2-*b*]carbazole-2,8-diyl)bis-(benzo[*d*]thiazole) (8h). Orange crystals, yield 950 mg (80%), mp 205-206 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* 8.3 Hz, 2H), 8.05 (d, *J* 8.3 Hz, 2H), 7.83 (d, *J* 7.6 Hz, 2H), 7.53 – 7.37 (m, 6H), 7.37 – 7.32 (m, 1H), 6.98 (s, 4H), 4.19 (s, 6H), 4.06 – 3.95 (m, 4H), 3.90 (s, 12H), 1.73 – 1.61 (m, 4H), 1.34 – 1.15 (m, 32H), 1.12 – 1.00 (m, 4H), 0.87 (t, *J* 6.8 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.6, 154.3, 144.2, 138.5, 134.5, 132.98, 132.95, 126.2, 125.0, 124.6, 123.8, 123.5, 123.3, 122.9, 122.8, 122.4, 121.5, 118.7, 109.0, 107.1, 61.2, 56.4, 44.8, 31.9, 29.62, 29.59, 29.5, 29.3, 27.0, 22.7, 14.1. Anal. Calcd for $C_{74}H_{86}N_4O_6S_2$: C, 74.59; H, 7.27; N, 4.70; Found: C, 74.66; H, 7.45; N, 4.63.

2,2'-(6,12-Bis(4-chlorophenyl)-5,11-didodecyl-5,11-dihydroindolo[3,2-*b*]carbazole-2,8-diyl)bis(benzo[*d*]-thiazole) (8i). Orange crystals, yield 1 g (93%), mp 237-238 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* 8.3 Hz, 2H), 8.05 (d, *J* 7.9 Hz, 1H), 7.89 (d, *J* 7.9 Hz, 1H), 7.77 (d, *J* 8.3 Hz, 4H), 7.68 (d, *J* 8.3 Hz, 4H), 7.50 – 7.44 (m, 2H), 7.41 – 7.30 (m, 4H), 6.97 (d, *J* 1.6 Hz, 2H), 4.10 – 3.88 (m, 4H), 1.67 – 1.53 (m, 4H), 1.30 – 1.11 (m, 32H), 1.06 – 0.94 (m, 4H), 0.88 (t, *J* 6.8 Hz, 6H). ^{1}H NMR (400 MHz, C_6D_6) δ 8.68 (dd, *J* 8.6, 1.6 Hz, 2H), 8.26 (d, *J* 8.0 Hz, 2H), 7.63 (d, *J* 7.5 Hz, 2H), 7.49 (d, *J* 8.3 Hz, 4H), 7.44 (d, *J* 1.6 Hz, 2H), 7.36 (d, *J* 8.3 Hz, 4H), 7.24 – 7.19 (m, 2H), 7.14 – 7.12 (m, 2H), 7.06 – 7.00 (m, 2H), 3.83 – 3.66 (m, 4H), 1.49 – 1.39 (m, 4H), 1.38 – 1.28 (m, 24H), 1.25 – 1.18 (m, 4H), 1.09 – 1.00 (m, 4H), 0.96 – 0.90 (m, 6H), 0.89 – 0.81 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.5, 153.8, 144.1, 136.5, 135.2, 134.6, 132.8, 131.7, 129.8, 126.2, 124.9, 124.6, 123.8, 123.1, 122.9, 122.7, 122.5, 121.4, 117.5, 108.9, 44.7, 31.9, 29.7, 29.64, 29.56, 29.4, 29.2, 29.1, 29.0, 26.8, 22.7, 14.1. Anal. Calcd for $C_{68}H_{72}Cl_2N_4S_2$: C, 75.60; H, 6.72; N, 5.19; Found: C, 75.65; H, 6.72; N, 5.32.

2,2'-(5,11-Didodecyl-6,12-di(thiophen-2-yl)-5,11-dihydroindolo[3,2-*b*]carbazole-2,8-diyl)bis(benzo[*d*]-thiazole) (8j). Orange crystals, yield 930 mg (91%), mp 225-226 °C. ^{1}H NMR (400 MHz, C_6D_6) δ 8.81 (dd, *J* 8.7, 1.6 Hz, 2H), 8.20 (d, *J* 7.8 Hz, 2H), 7.70 – 7.57 (m, 4H), 7.42 (d, *J* 4.4 Hz, 2H), 7.27 – 7.18 (m, 8H), 7.07 – 7.01 (m, 2H), 3.96 – 3.76 (m, 4H), 1.65 – 1.49 (m, 4H), 1.39 – 1.20 (m, 28H), 1.19 – 1.10 (m, 4H), 1.05 – 0.95 (m, 4H), 0.92 (t, *J* 6.7 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.8, 153.2, 144.3, 138.0, 134.3, 128.6, 128.3, 128.2, 128.0, 126.2, 125.4, 124.8, 124.6, 123.8, 123.2, 122.6, 122.4, 121.4, 111.5, 109.2, 44.8, 31.9, 29.7, 29.57, 29.56, 29.39, 29.35, 29.31, 29.26, 26.9, 22.7, 14.1. Anal. Calcd for $C_{64}H_{70}N_4S_4$: C, 75.10; H, 6.89; N, 5.47; Found: C, 75.20; H, 6.70; N, 5.66.

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